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A New form of Rotating
Cathode for the Electrodeposition
of Metals

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A NEW FORM OF ROTATING CATHODE
FOR THE ELECTRODEPOSITION
OF METALS

BY

BRADLEY CHARLES GARDNER

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

IN THE

COLLEGE OF SCIENCE

OF THE

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION[#] BY

Bradley Charles Gardner

ENTITLED A New Form of Rotating Cathode

For the Electrodeposition of Metals,

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor of Science



HEAD OF DEPARTMENT OF Chemistry.

The work of this thesis was done under the immediate direction
of Professor A. T. Lincoln.



A NEW FORM OF ROTATING CATHODE FOR
THE ELECTRO-DEPOSITION OF METALS.

The fact that some metals become superficially coated with other metals when plunged into suitable solutions was known to the ancients, who often coated their iron swords with copper by dipping them into copper solutions, but it was not until the beginning of the nineteenth century that metals were deposited from their solutions by means of an electric current. The first attempts at the electrolytic deposition of the metals was made by Cruikshanks in 1801, and was entirely qualitative, although he suggested that a quantitative determination of some of them might be made by use of an electric current. In the same year Wollaston discovered that by introducing a strip of silver, in contact with zinc, into a copper sulphate solution, he could obtain a coating of copper on the silver, which was so adherent that it could be burnished. The attention of many investigators was now directed towards this field and numerous experiments were made. In 1830 Becquerel observed that lead and manganese often separated, not as metals at the negative pole, but as oxides at the positive electrode, thus being separated from the other metals. One of the first discoveries in this field that was of technical importance, was



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made in 1839, when three chemists independently described the process of electrotyping. These three were Jacobi of St. Petersburg, and Spencer and Jordan in England. However, Jacobi's publication bears the earliest date.

The application of the art of electrotyping to the requirements of the printer was made practicable by Murray's discovery that moulds of non-conducting materials could be made to take a deposit of copper, by first brushing them over with plumbago. In this same year (1840) the first newspaper printed from an electrotyped block was published by the London Journal.

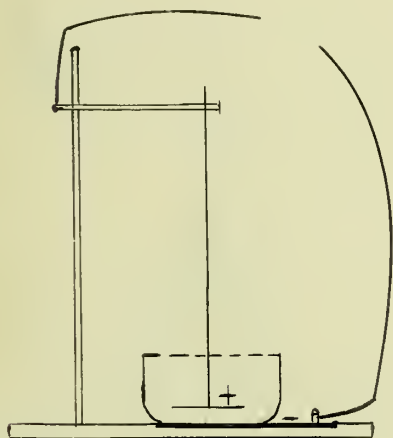
Though it was now known how to produce heavy deposits of copper, those of gold and silver could be obtained only in very thin layers. In 1840, however, Wright employed the solutions of the metallic cyanides in potassium cyanide, and found that the deposits produced from these solutions could be developed to any desired thickness. These double cyanide solutions are still used in most plating works. In the same year (1840) nickel was deposited from a solution of nickel nitrate, and in 1841 Mr. Alfred Smee published his experiments in the deposition of antimony, platinum, gold, silver, iron, lead, copper and zinc. Two years later Dr. Ruolz first succeeded in depositing metallic alloys, such as brass, from the solutions of the mixed salts. From this time on many similar inventions were patented, but they are not sufficiently distinctive to warrant recording them in detail, and from the work mentioned it may be seen that nearly all of the common metals had been deposited electrolytically as early as 1845. Does it not seem

strange that no quantitative determinations were reported until about twenty years later?

The field of quantitative investigation was first entered by Walcott Gibbs in 1864, who published an account of the electrolytic determination of copper, and nickel and also the descriptions of the methods for the determination of silver, bismuth, lead and manganese. This article was quickly followed by one written by Luckow, in which the writer claimed to have determined copper electrolytically as early as 1860.

The development of quantitative electrolysis was very rapid, due no doubt to the large amount of data which had been collected by the earlier investigators in the qualitative field. Zinc was determined from a solution of zinc sulphate containing an excess of ammonium acetate, by Parodi and Mascagni in 1877. Richert first accurately determined manganese

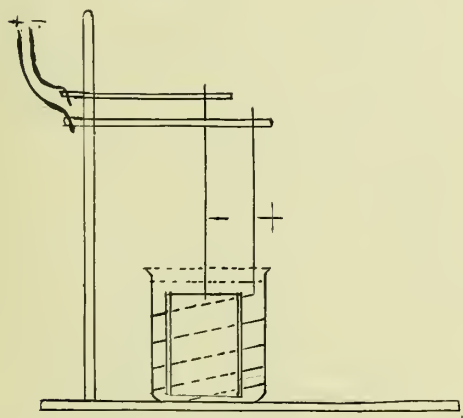
electrolytically in 1879, when he found that it could be completely separated at the positive electrode in the form of an oxide from solutions of its nitrate. In 1880 Fresenius and Bergman found that nickel and cobalt were best deposited from their sulphate solutions in the presence of an excess of ammonia and ammonium sulphate.



As the methods of manipulation in most of the above determinations are quite similar it will only be necessary to describe two of them. In the first method the solution to be

electrolyzed is placed in a previously weighed ^{platinum} dish of about 150 c.c. capacity, and the dish is connected with the negative pole of the source of electricity, either by means of a clamp, or by placing it on a copper plate which is in the circuit. The anode is generally a flat disc of platinum or a coil of platinum wire, and is connected as in the sketch on previous page. The strength of the current is regulated by changing the external resistance "R" or by varying the distance between the electrodes. When the deposition is complete the solution is removed by means of a siphon, and distilled water is added while the current still passes. After washing several times the current is shut off and the deposit is dried and weighed.

In the second method the deposition is made in a glass or porcelain beaker and two platinum electrodes are used. The cathode is generally in the form of a cylinder or a cone,



while the anode is a larger cylinder or a coil of platinum wire. In making a determination the solution is placed in the beaker and the two electrodes are arranged as in the opposite sketch, using care to see that all points on the surface of the cathode are

nearly equidistant from the anode. When the deposition is complete the solution is removed as directed above, and after drying the cathode is weighed. As the weight of the cathode alone is known the weight of the deposit is obtained by difference.

Both of these methods give very accurate results, but they also have their disadvantages as well. One of the principal objections is the time required to obtain the deposit. In the case of copper, which is one of the most easily deposited metals, from four to twelve hours are required to completely deposit the metal. Of course it would be an easy matter to pass a strong current through the solution and throw^{out} the metal in a short time, but when this is done the metal comes down in a soft spongy form, and it is almost impossible to weigh it as it does not adhere to the cathode. Another disadvantage is that even when a current of low density is used, there is a tendency for the metal "to tree" at the edges of the cathode, and at the points where the current density is the greatest. If the deposit trees there is danger of losing some of the metal while washing and weighing it. In both of these methods the bubbles of gas escaping at the electrodes are liable to cause a loss through spattering unless especial care is taken. The first of these objections is the most important however.

The fact that the electrolytic deposition of metals is hastened and the deposit made more uniform when the electrolyte is agitated, is recognized in the plating business, and consequently the baths are agitated by mechanical stirrers. This same principle has recently been applied to the quantitative determination of the metals. Wimmenaur(Zeit. fur Anorg. Chem. 27 - 1(1901)) was the first to stir the electrolyte. He found that when bismuth was determined in the ordinary electrolytic way it separated out at both poles, at the cathode as the metal

and at the anode as the peroxide. He also discovered that the peroxide was not formed if the anode was rotated, and he explained it by the assumption that the rotation brings the peroxide into contact with the dilute nitric acid in the electrolyte which dissolves^{it} at once. When the anode is at rest a protective film of gas forms about it and prevents the solution of the peroxide. The principal objection to his method is that it is too involved and cannot be readily duplicated.

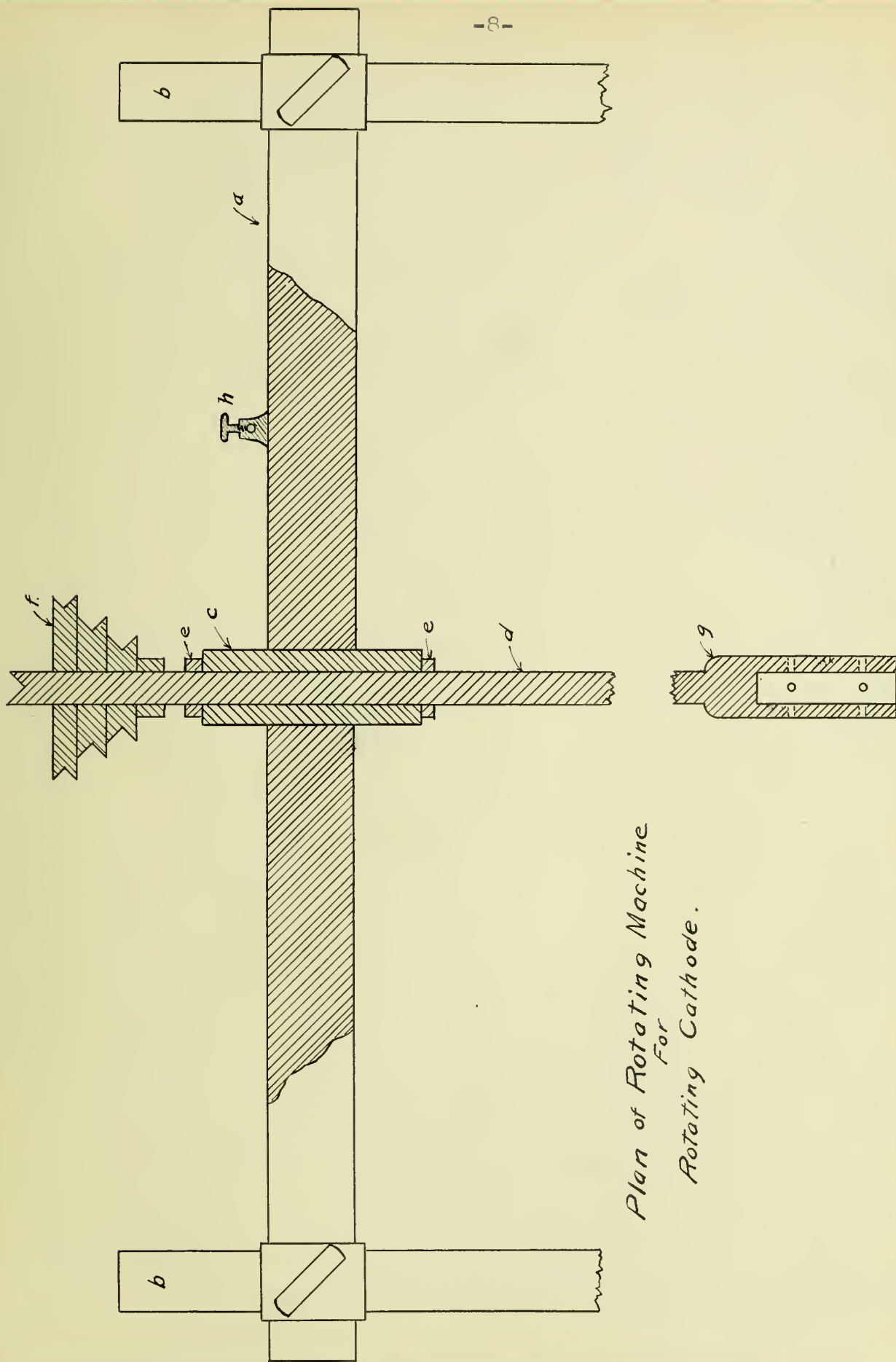
Gooch and Medway (Am. Jour. Sci., Series 4-15, 320--1903) published the first article on the use of the rotating cathode in the electrolytic determination of metals. In their manipulation they used as a cathode an ordinary platinum crucible rotating at a speed of from 600 to 800 revolutions per minute. The crucible is driven by a small electric motor, which is fastened so that its shaft is vertical. The crucible is fixed to this shaft by pressing it over a rubber stopper which is bored centrally and fitted tightly on to the end of the shaft. To secure electrical connection between the crucible and the shaft a small strip of platinum is soldered onto the shaft and bent upwards along the side of the stopper, thus putting the shaft in contact with the inside of the crucible. The solution to be electrolyzed is placed in a small beaker, which is adjusted so that the crucible (cathode) dips into the solution. The anode used is a small platinum plate. The first attempts were made with the deposition of copper from a solution of the sulphate and were very successful, as the complete deposition of from .1 to .25 g. of copper was accomplished in from 15 to

20 minutes. Silver and nickel were also deposited very rapidly and accurately.

Shortly after this F.F.Exner (Jour. Am. Chem. Soc. 25 - 896(1903)) described his experiments using a rotating anode. His method was quite simple and was as follows: the solution to be electrolyzed was placed in a platinum dish which acted as the cathode. The anode was a spiral of heavy platinum wire about two inches in diameter and was rotated at a speed of from 500 to 600 revolutions per minute. In this way he was able to use a great deal higher current density and still obtain deposits that were firm and adherent, and he could completely deposit the metal in a few minutes. Exner made determinations of copper, nickel, silver, bismuth, cadmium, iron, lead, tin, gold, and antimony with considerable success. His results have lately been verified by Edgar F. Smith and others at the University of Pennsylvania.

It was the work of these investigators that suggested the idea that if a cathode with considerable surface was constructed, and rotated very rapidly in a solution of small volume, the deposition would be very rapid and convenient. It was with this idea in mind that this research was begun.

Some preliminary determinations of copper, silver, and nickel were made using the apparatus of Gooch and Medway, and also with stationary electrodes, and satisfactory results were obtained. However it was very difficult to regulate the small motor, and so a new rotating machine was devised.



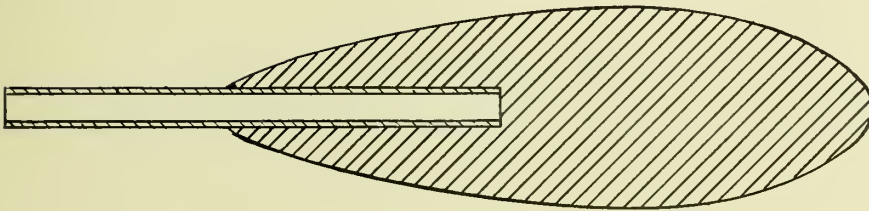
*Plan of Rotating Machine
For
Rotating Cathode.*

The cross bar "a" is of three-fourths inch steel turned round at the ends so that it may be fastened to the uprights "b, b" by ordinary clamps. It is twelve inches long. In the middle of the bar is the brass bearing "c". This bearing is two inches long and its outside diameter is one-half inch. It has a one-quarter inch bore through the center in which the spindle "d" rotates. This spindle is eight inches long and one-quarter inch in diameter and is turned to fit the hole in the bearing. The spindle carries two movable lugs "e, e" which permit it to be adjusted to different lengths. At the top of the spindle is the pulley cone "f" which is also adjustable, and at lower end is the chuck "g". The electrode is held in the chuck by six set screws. The electrical connection with the electrode is made by means of the binding post "h", the current passing through the spindle to the electrode. The conical depression in the top of the spindle permits the easy adjustment of the speed counter. The power to rotate the spindle is obtained from a 1/8 h.p. Emerson motor(110 volts, 1100 r.p.m.) which has on its shaft a cone of three pulleys, so by varying the pulleys used on the motor and the spindle the speed may be varied from 1100 r.p.m. to 4400 r.p.m. Even at the highest speed very little vibration is felt as it is taken up by the heavy base.

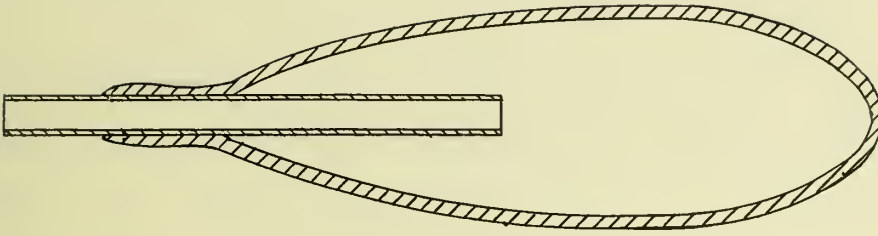
The next problem was the construction of a suitable

electrode, and finally it was decided to make one in the form of an ellipsoid, as the rounded surfaces would tend to cause an equal distribution of the current, and because one of this shape could be rotated conveniently. How to construct this electrode of the proper size, weight and material was a serious question and finally became the point of the research. It is evident that the electrode must be made of platinum in order that the metals deposited on it may be dissolved off without the electrode itself losing weight. The first idea was to electroplate copper on an aluminum casting and then plate platinum on the copper. This idea was followed out by B. D. Ingles but the resulting electrode weighed 90 grams and was therefore altogether too heavy. It was then decided to cast the electrode in wax about a hollow brass tube (See sketch). In order to ^{accomplish} this the melted wax was poured into a plaster of Paris mold of the desired shape and after cooling for some hours the electrode was removed from the cast. The surface of the wax was made conducting by covering it with graphite, then copper was deposited on it, and finally platinum was plated on the copper. When the electrode was finished the wax was melted and poured out through the hollow brass tube.

It was desired to make the electrode of "Woods metal" or of some other alloy with a low melting point, but it was not convenient to obtain enough of the alloy to form the casting. Considerable difficulty was encountered in obtaining a suitable wax casting but one was finally obtained by making the form somewhat larger than desired and then turning it down on a



CROSS SECTION OF WAX ELECTRODE
SHOWING POSITION OF BRASS TUBE.



CROSS SECTION OF ELECTRODE
SHOWING COPPER SHELL AFTER
REMOVAL OF WAX.

lathe. Several different copper solutions were tried, (a) strong copper sulphate solution with a little sulphuric acid, (b) the same solution containing a little nitric acid, (c) the same solution containing an excess of potassium cyanide. The first solution gave the best results, when it was decomposed by a current of three to four volts potential, and two amperes, N.D.₁₀₀. During the deposition of the copper the electrode was frequently polished and then roughened with emery in order to obtain a close grained deposit. When about thirty-five grams of copper had been deposited, the electrode was carefully polished with silica and cleaned with a solution of KOH, then with dilute sulphuric acid, and finally thoroughly washed with water. The electrode was now ready for the platinum bath.

The platinum bath used is the one recommended by Roseleur. The directions for making it are as follows: four grams of platinum chloride are dissolved in 100 c.c. of water, and the solution is thoroughly mixed with a solution of twenty grams of ammonium phosphate in 200 c.c. of water. This mixture is added to one hundred grams of acid sodium phosphate in 700 c.c. of water, and the whole solution is then boiled until ammonia is no longer given off. During boiling the volume is kept constant by replacing the water removed by evaporation. This solution is electrolyzed with a current of two amperes N.D.₁₀₀, potential three or four volts, and gives the best results when heated to 60° - 70° C. A spiral of heavy platinum wire is used as an anode. The deposit from this solution is of a dull gray color, but it is easily polished, yielding a

bright metallic finish.

The principal difficulty encountered in plating the electrode with platinum was in obtaining an adherent deposit, and in order to do this the electrode must be perfectly clean.

SUMMARY.

It has been shown that a hollow copper ellipsoidal electrode may be made and plated with platinum, and used in place of the usual platinum electrodes. The advantages of this electrode are that it permits rotation at a very high speed without loss of the liquid, and that it affords a convenient cathode for the rapid electrolytic deposition of metals, and further it may be made in any laboratory at a small cost.

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